UDC 666.3:620.17:519.2

STRUCTURE AND STRENGTH OF COMPOSITE CERAMIC MATERIALS

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Translated from *Steklo i Keramika*, No. 2, pp. 9 – 12, February, 2010.

A slip-casting technology for preparing two- and three-fraction composite ceramic materials is examined. Their structural parameters are investigated. The strength of the materials is determined. Anomalous behavior of the material strength is found near the percolation threshold (filler content — 16%); this is a structural effect.

Key words: ceramic, composite materials, filler, structure, strength.

The development of composite materials is one of the directions given priority in the development of ceramics. This is due to advances in the technology for manufacturing ceramic articles [1 – 4] and the study and monitoring of the structural parameters of such materials [5]. For this reason, structural studies of composite materials for the purpose of improving their operating characteristics are topical. In the present work, the structural and strength properties of samples of two- and three-fraction ceramic composite materials manufactured by the slip-casting methods are studied.

The composite materials studied in this work are fabricated from refractory fill on a porcelain matrix (the powder mix for PFL-1F electroporcelain (GOST 20419) was used). The characteristics of the initial PFL-1F mix were as follows: moisture content no more than 6%, residue on a No. 0063 sieve no more than 1.8%, total shrinkage no more than 14%, firing temperature 1280 – 1300°C, and bending strength of the fired sample at least 55 MPa.

The chemical composition of the PFL-1F is as follows (wt.%): 67.0 SiO_2, 21.5 Al_2O_3, 0.55 Fe_2O_3, 0.6 TiO_2, 0.4 CaO, 0.3 MgO, 2.3 K_2O, 1.4 Na_2O, and 5.8 other.

Commercial 60 – 120 μm silicon carbide SiC with pycnometric density 3.2 g/cm^3 and 0.5 – 1.0 and 0.2 – 5.0 mm fireclay with pycnometric density 2.6 g/cm^3 [1] were used as the filler.

The samples of the composite materials were fabricated with a prescribed content of SiC (60 – 120 μm) and fireclay. Their compositions are presented in Table 1. A batch of samples was made from pure porcelain for checking and comparing the measured properties. The samples were prepared by slip casting in a gypsum mold followed by drying and firing at 1280°C.

To prevent the slip from stratifying during casting, which makes the material nonuniform and the appearance of cracks on the sample more likely, the relative moisture content of the slip was adjusted in the range 22 – 25% (the fluidity of the slip was monitored with an Engler viscosimeter). On the basis of the data of [2, 3] the slip was liquefied with liquid glass (0.22 – 0.28%) and sodium pyrophosphate (0.3%). The hardness of the water was checked and confirmed to be 11 – 12 mg · eqv/liter). The relative moisture content of composition 4 was determined pycnometrically and that of other slips by weighing following by drying in a dessicator [1].

The casting slip was prepared by adding water and electrolytes to the porcelain powder mix followed by mixing and maturing for 1 – 2 h. Next, silicon carbide and fireclay were added to the slip, which was mixed once again and allowed to stand (mature) for at least one day. The cast samples were

TABLE 1.

Composition	Content, vol.%		
	porcelain	SiC	fireclay
1-1	88	12	–
1-2	86	14	–
1-3	84	16	–
1-4	82	18	–
1-5	80	20	–
1-6	70	30	–
1-7	60	40	–
1-8	50	50	–
2-5	50	35	15
2-6	50	30	20
3-5	50	35	15
3-6	50	30	20
4	100	–	–

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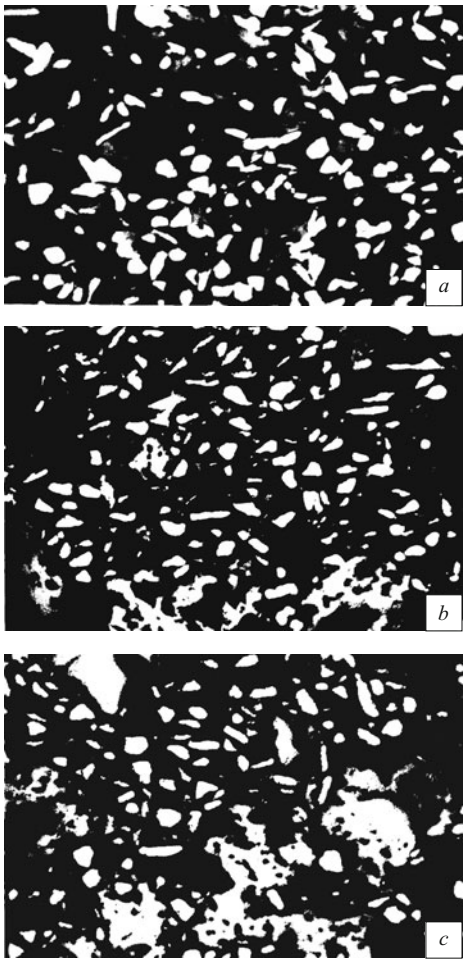

Fig. 1. Structure of the ceramic composite materials (reflected light, × 70): *a*) composition 1-6 (filler SiC); *b*) composition 2-6 (filler SiC and fireclay fraction 0.5 – 1 mm); *c*) composition 3-6 (filler SiC and fireclay 0.2 – 0.5 mm).

dried to a constant paste and fired in a production furnace at 1320°C.

The structural characteristics of the ceramic composites were determined by microstructural analysis. Figure 1 displays sections of samples of the materials. SiC as well as SiC combined with fireclay were used as filler.

TABLE 2.

Sample	Structural parameters				
	Grain content, vol.%		Average grain size, μm		Average distance, μm, between SiC grains
	SiC	fireclay	SiC	fireclay	
1-1	13.0	–	65.5	–	398.2
1-2	13.6	–	66.5	–	415.5
1-3	16.2	–	64.1	–	334.0
1-4	18.0	–	66.8	–	283.7
1-5	19.8	–	64.4	–	252.1
1-6	30.6	–	66.0	–	145.9
1-7	38.5	–	61.7	–	101.5
1-8	46.8	–	61.4	–	68.3
2-5	35.2	12.8	66.4	730.0	79.2
2-6	29.6	19.3	64.5	780.3	91.8
3-5	34.3	15.0	62.3	260.7	73.2
3-6	29.1	19.5	65.2	281.9	77.3

The crystalline phase of the samples consists predominately of silicon carbide grains with fragmental elongated shapes. The SiC distribution in the samples 1-1 – 1-8 is uniform (the coefficient of variation k is less than 9%). For example, for sample 1-6 the computed volume content of SiC was 30.6% with k = 7.8%.

The distribution of the fireclay in the samples is less uniform. Thus, for sample 2-6 the volume content of the fireclay was 19.3% with k = 14.5%.

The maximum grain size of the fireclay was 1000 – 1200 μm in the samples 2-5 and 2-6 and 500 – 600 μm in samples 3-5 and 3-6. The boundaries of the fireclay grains are corroded; cracks and pores ranging in size from 5 – 10 to 100 – 150 μm are present inside the grains. The quantitative structural characteristics of the composite materials of the samples are presented in Table 2, and histograms of the dis-

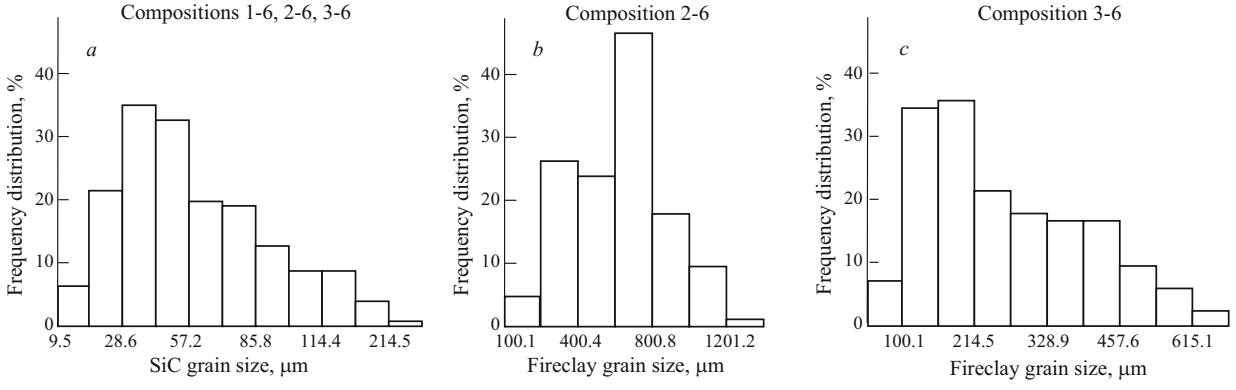

Fig. 2. Size distribution of the filler grains in the compositions: *a*) SiC in compositions 1-6, 2-6, and 3-6; *b* and *c*) fireclay in compositions 2-6 and 3-6, respectively.

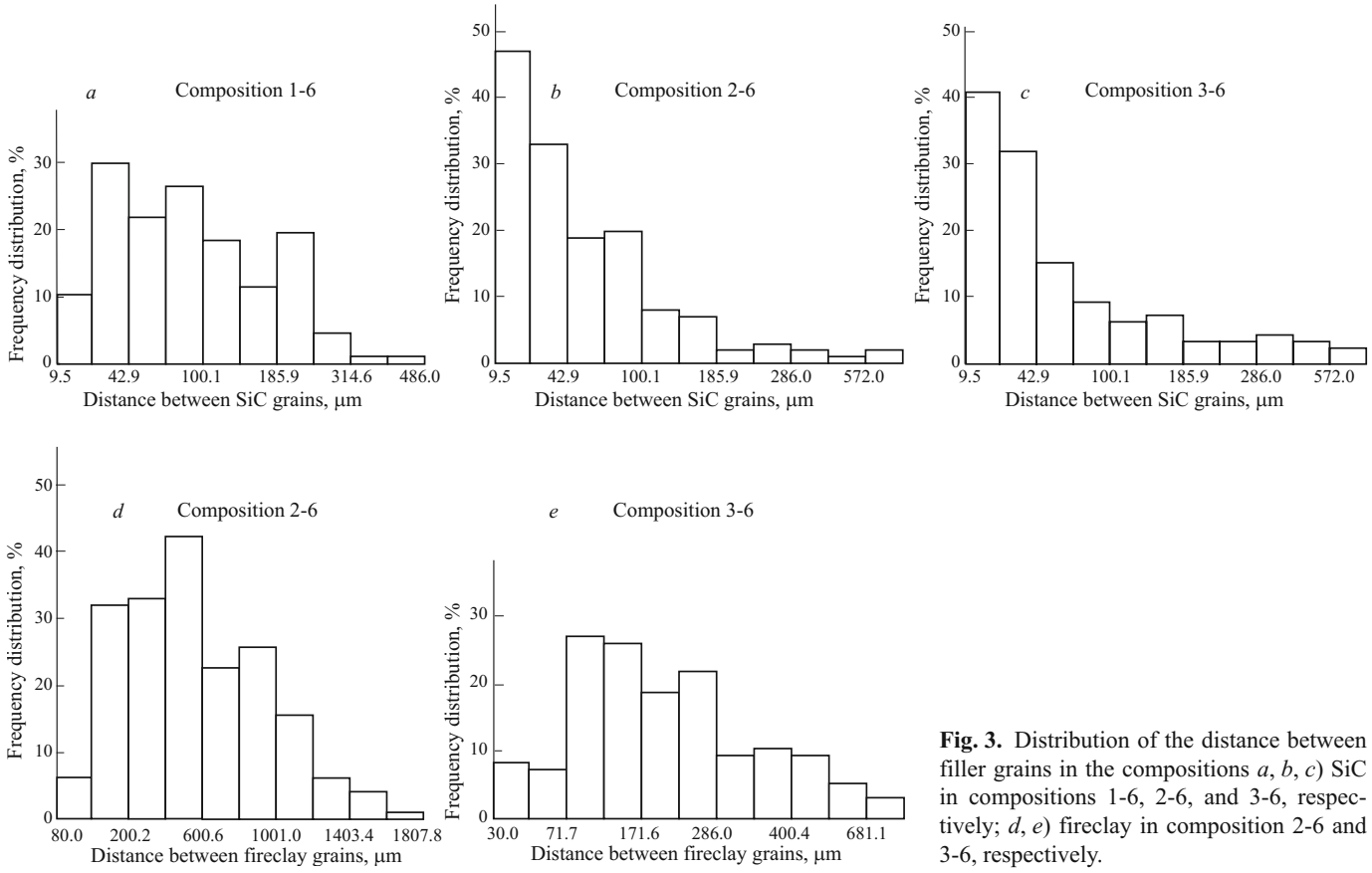

Fig. 3. Distribution of the distance between filler grains in the compositions *a*, *b*, *c*) SiC in compositions 1-6, 2-6, and 3-6, respectively; *d*, *e*) fireclay in composition 2-6 and 3-6, respectively.

tribution of SiC and fireclay grains as well as the distances between then are presented in Figs. 2 and 3.

The bending strength of the composite materials was evaluated from the value of the breaking bending moment of 80 × 20 × (6 – 10) mm beams. The strength was determined on a RM-250 rupture machine by a three-point scheme; the width and height of the beams at the location of the break were measured after the breaking load was determined.

A statistical analysis of the experimental data on the strength of the material was performed using the method of [6]. Aside from the arithmetic mean $\bar{x}$, the variance S_x^2, and the standard deviation S_x, the error was determined with confidence probability $\alpha = 0.95$ or significance level 0.05 (Table 3).

Let us analyze whether or not this technological process conforms to percolation theory. For this, we shall use the typical percolation dependence for the conductivity or strength σ [5]:

$$\delta = \delta_0 [(V - V_{cr})/(1 - V_{cr})]^t,$$

where σ_0 is the strength or electric conductivity of pore-free material; V is the volume concentration of the solid phase; V_{cr} is the critical volume concentration of the solid phase ($V_{cr} = 0.157$ can be used for spherical particle); and, t is the critical index (for a three-dimensional system $t = 1.8$).

The expression was used to calculate the initial strength δ_0 of pore-free material and, using the value so obtained, the theoretical values of the strength for different value of the

TABLE 3.

Composite	Bending strength, MPa	Standard deviation	Error, %, with $\alpha = 0.95$
1-1	39.17	1.949	15.1
1-2	44.64	0.606	4.1
1-3	48.29	1.333	8.4
1-4	46.00	2.037	13.5
1-5	46.15	0.251	16.5
1-6	41.22	2.191	16.2
1-7	28.44	1.701	18.1
1-8	43.29	2.498	17.5
2-5	29.42	0.557	5.7
2-6	27.59	0.510	5.6
3-5	32.38	1.991	18.6
3-6	31.66	1.624	15.0
4	50.46	1.360	8.2

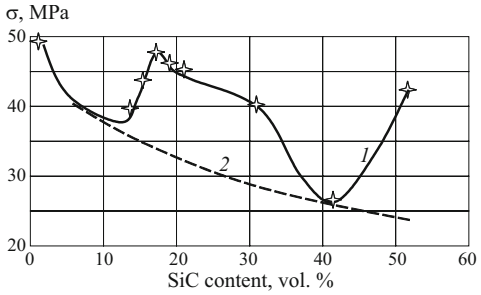

Fig. 4. Bending strength of the samples: *1*) experimental data; *2*) theoretical dependence of the strength on the filler content according to the expression presented.

porosity. Figure 4 displays the experimental values of the bending strength of the samples. As one can see, the strength of the material (16% SiC content) increases anomalously near the percolation threshold, i.e., a structural effect occurs as a result of the formation of an infinite cluster from the silicon carbide particles which are in contact with another. The strength of the composites also increases anomalously in the 50% SiC content range. This could be due to the thinning of the porcelain interlayers between the silicon carbide grains and the corresponding increase of the strength characteristics of the matrix phase (binder).

Cup molds were used to show the possibility of using the technology described above to produce composite articles with a complex (hollow) shape for different purposes (for electric heaters or heat-resistant articles which are safe for human health). Since the filler greatly decreases the strength of dry articles, to use the simplest method of glazing (dipping or pouring), the articles were strengthened by pre-sintering. In this process free and crystal bound water is removed from the porcelain paste, carbon and organic inclusions are burned out, and a small quantity of glass phase is formed. As a result, the mechanical strength is increased to 1 MPa and higher, which is adequate for glazing by dipping.

In summary, the anomalous increase of the strength of the material at the percolation threshold (16% SiC content) is a consequence of a structural effect — formation of an infinite cluster form silicon carbide particles in contact with one another.

An anomalous increase of the strength of the material at 50% SiC content was also observed. Apparently, this increase is due to thinning of the porcelain interlayers between the silicon carbide grains, a change in this connection of its properties (size effect), and a corresponding improvement of the strength properties of the matrix phase.

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